THE INFRARED ABSORPTION SPECTRUM OF CARBON MONOXIDE

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A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY AT THE OHIO STATE UNIVERSITY

By

ERWIN FOSTER LOWRY

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During the past ten years a constantly increasing amount of work has been done on the absorption spectra of various gases in the near infra-red. Its purpose has been two fold, namely, to test the possibility of extending the application of the quantum theory to the rotational and vibrational energy of the molecule and to endeavor by this means to throw added light on molecular structure and dimensions.

Bjerrum[1] showed that the band spectra in the near infra-red were due to a combination of rotational and vibrational frequencies, that is,

$$\nu = \nu_0 \pm \nu_r$$

where ν_0 is the frequency of vibration of the oscillator and ν_r its frequency of rotation. Thus if the rotational frequencies be quantized a series of lines may be expected, spaced symmetrically about the frequency $\cdot\nu_0$. If ν_r be quantized a series of such bands may be predicted, the so-called harmonics already found in the spectra of several gases. Burmeister[2] has investigated a number of gases and found that the band spectra of most of them were doublets. From considerations based on the classical statistical mechanics Kemble[3] has derived the expression

$$I = \frac{RT}{4\pi^2 \nu_r^2 N}$$

for the moment of inertia of a diatomic molecule based on the rotational frequency ν_r obtained from the position of the maxima of the Burmeister doublets, where R is the gas constant, T the absolute temperature, N Avogadro's number, and $2\nu_r$ the difference in frequency of the two maxima. With the aid of a spectrometer of moderate resolving power, Eva von Bahr[4] was able to obtain twelve maxima in the absorption spectrum of HCl. Later, Imes[5] in a very fine piece of work extended this number to 24, twelve pairs grouped about the frequency ν_0 as well as a similar separation of the components of the bands of HBr and HF. This number of maxima for HCl has been still further extended by Colby and Meyers[6] and others. Eva von Bahr[7] and more recently Sleator[8] have

[1] Nernst Festschrift, p. 90; 1912.
[2] Verh. d. D. Phys. Ges., p. 608; 1913.
[3] Phys. Rev. *8*, No. 6, p. 696; 1916.
[4] Verh. d. D. Phys. Ges., *15*, p. 1150; 1913.
[5] Astrophys. Jour., *50*, No. 4, p. 251; 1919.
[6] Astrophys. Jour., *53*, No. 4, p. 300; 1921.
[7] loc. cit.
[8] Astrophys. Jour., *48*, No. 2, p. 125; 1918.

obtained very complex curves for the spectrum of water vapor. Barker[9] has resolved the spectrum of carbon dioxide at 4.3μ into a doublet and its harmonic at 2.7μ into a pair of doublets which give considerable evidence of fine structure. Obviously little can be hoped for at the present time in the interpretation of these results on tri-atomic molecules due to the difficulties in the mathematics involved.

From theoretical considerations carbon monoxide should give a spectrum very similar to that of the halogen acids and the present work was undertaken in the hope that additional evidence might be obtained for the application of quantum theory to molecular behavior. Ängstrom[10] located this band at 4.56μ, Coblentz[11] found the center of the band at 4.59μ, while Burmeister[12] resolved it into a doublet with maxima at 4.60μ and 4.72μ giving the center of the band at 4.67μ. Ängstrom found the first harmonic at 2.48μ while both Coblentz and Burmeister gives its location as 2.35μ.

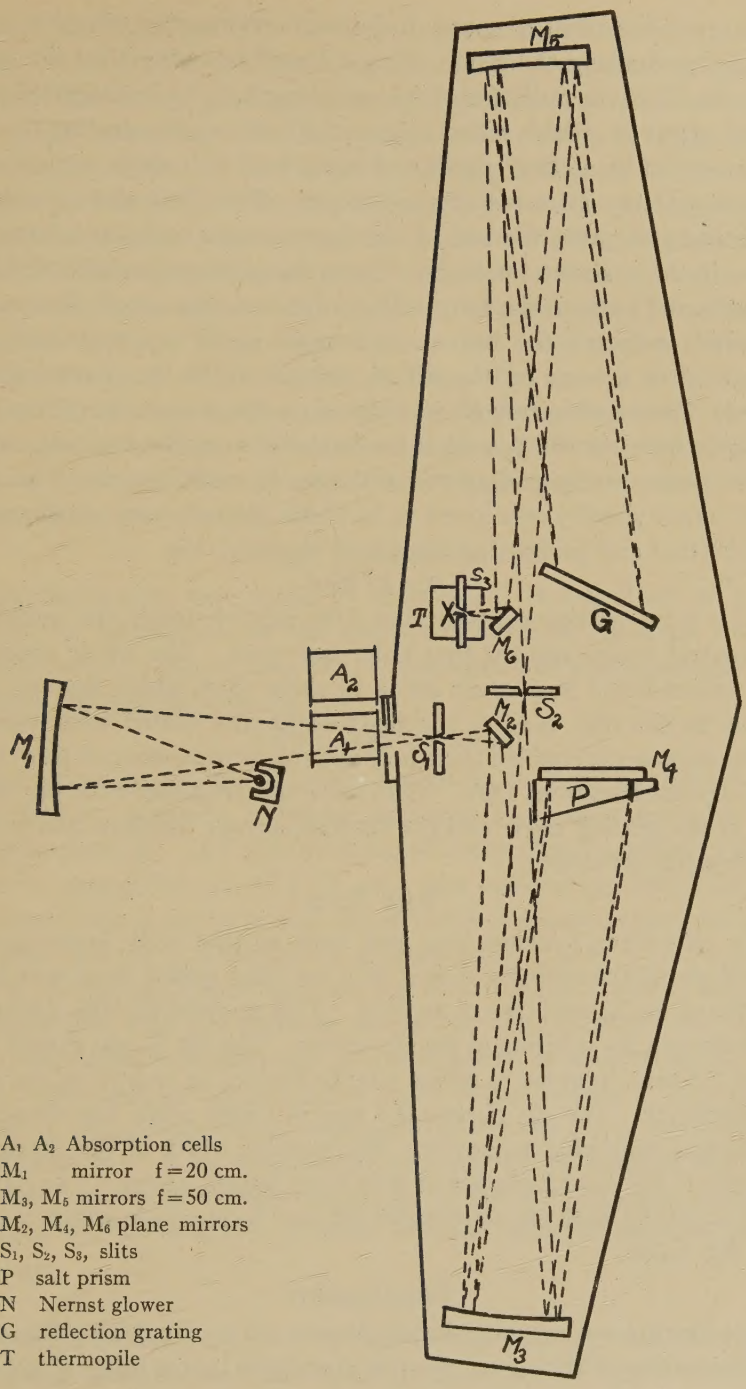
THE APPARATUS

The apparatus was similar to that used by Sleator in his work on water vapor and by Imes on the halogen acids, which has the advantage of bringing to bear on the infra-red region a much higher resolving power than had heretofore been possible.

THE SPECTROMETER

Fig. 1 is a diagram of the spectrometer which is of a special combination prism-grating type. The radiation from the source, a Nernst glower, is brought to a focus on the slit S_1 by the concave spherical mirror M_1. It is then reflected approximately at right angles by the small plane mirror M_2 to the concave mirror M_3, which is placed at a distance equal to its focal length from the slit S_1. This mirror throws a parallel beam of radiation on the rock salt prism P which has a refracting angle of about 15° and a surface of (15 cm)^2 and is backed by the plane mirror M_4. The beam is thus caused to retrace its path thru the prism and back to the mirror M_3 which brings the spectrum to a focus on the slit S_2. This arrangement makes use of the well known principle of autocollimation, enabling any desired portion of the spectrum to be brought to a focus on the slit by simply rotating the prism. The purpose of this

[9] Astrophys. Jour., *55*, No. 5, p. 391; 1922.
[10] Öfv. af Kongl. Vet. Akad. Förh., *46*, p. 549; 1889.
[11] Investigations of Infra-red Spectra, pts. 1-2, p. 17.
[12] loc. cit.



A_1 A_2 Absorption cells
M_1 mirror f = 20 cm.
M_3, M_5 mirrors f = 50 cm.
M_2, M_4, M_6 plane mirrors
S_1, S_2, S_3, slits
P salt prism
N Nernst glower
G reflection grating
T thermopile

FIG. 1. *The Spectrometer.*

prism spectrometer is of course to prevent overlapping of orders on the grating by limiting the range of wave lengths passing thru the slit S_2. From the slit S_2 the radiation of the wave lengths to be investigated passes to the mirror M, which reflects a parallel beam to the grating G. This was mounted on a circle capable of being read to a single second of arc by means of two micrometer microscopes. The circle and microscopes were arranged under the bed of the spectrometer with the microscopes placed in the horizontal position. From the grating the diffracted beam was reflected back to the mirror M_5 and then to the small plane mirror M_6 which reflected the beam at an angle of 90° approximately and brought it to a focus on the slit S_3, behind which the thermopile was placed. The small mirror M_6 was placed as close as possible to the beam emerging from the slit S_2 so that the angle between the incident and diffracted beams at the grating was of the least possible value. This angle as measured visually was found to be 1° 10′ giving a very small amount of distortion and permitting the use of the equation

$$\lambda = 2g \sin\theta$$

where g is the grating constant and θ the angle between the position of the central image and the first order spectrum. The whole spectrometer was enclosed in a cover made of sheet iron which was set in a groove in the iron base of the instrument and sealed with vaseline. This arrangement enabled the whole apparatus to be washed thoroughly with dry air free from CO_2. The entire spectrometer with the exception of the grating circle and the thermopile was designed and built in the department shop.

THE SLITS

The slits were 2 inches long and built so that both jaws could be moved simultaneously by means of a rotating milled head which was graduated in thousandths of an inch. This method has the advantage of preserving the position of the slit center. The slit S_1 was rather wide, about 1.5 mm, in order to admit a large amount of energy to the prism spectrometer. The slit S_2 was 0.5 mm in width while the thermopile slit S_3 was somewhat narrower. The angular width of the thermopile slit was 1′ 40″ and included at this wave length about 85 ängstroms. For part of the work the thermopile slit was decreased in width to about half this value.

THE GRATING

The grating was one very kindly loaned me by Dr. H. M. Randall of the University of Michigan, ruled on aluminum by the original Rowland

engine. It was of a modified echellete type, not all of the plane face having been cut away so that it furnished a very strong central image. Though only the one grating has been used in the course of the investigation, the closeness of the check which was made on the spectrum of HCl and the method of taking observations would seem to have eliminated any serious errors due to any peculiarity of the grating surface. The grating constant was determined by measuring θ for several maxima of the HCl band at 3.46μ and found to be 2887.6 lines per inch, which is the result to be expected by dividing the constant of the Rowland engine 14438 by 5, every fifth tooth on the wheel driving the screw having been used in cutting this grating. The central image was so intense that it was found necessary in determining the normal position of the grating to place a thick piece of plate glass in the path of the incident beam, the glass of course absorbing a large percentage of the energy at the wave length 3.5μ.

THE THERMOPILE

The thermopile was made by Coblentz. It consisted of twelve elements of bismuth-silver and had a resistance of 7.4 ohms. It was mounted directly behind the slit S_3 and insulated as well as possible from external thermal distubances.

THE GALVANOMETER

The galvanometer was of the du Bois-Rubens type, built by Siemens and Halske, resistance 10 ohms, and was hung in a specially built Julius suspension. At a scale distance of 3 meters and a period of 20 sec. it had a sensitivity of 5×10^{-11} amp. per millimeter deflection. At this sensitivity however it was too unstable for satisfactory work add was used thruout at a sensitivity of from 1 to 2×10^{-10}. The unsteadiness of the galvanometer has been the most serious source of difficulty in connection with the problem and it has been necessary to take all observations between midnight and morning on very calm nights. For some reason not accounted for, a slight breeze caused a very erratic motion of the galvanometer suspension and forced me to work only on windless nights. A solenoid control was devised by means of which the zero and consequently the sensitivity of the galvanometer could be adjusted by the observer without moving from his position at the telescope.

THE SOURCE

A Nernst glower connected to the 110 volt lighting circuit served as the source of radiation and was very stable in its action though no

special ballast was used to attain this end. The constancy of the galvanometer deflections throughout a night's work when the zero of the galvanometer was maintained at a constant position was adjudged to be sufficient evidence of this stability.

THE ABSORPTION CELL

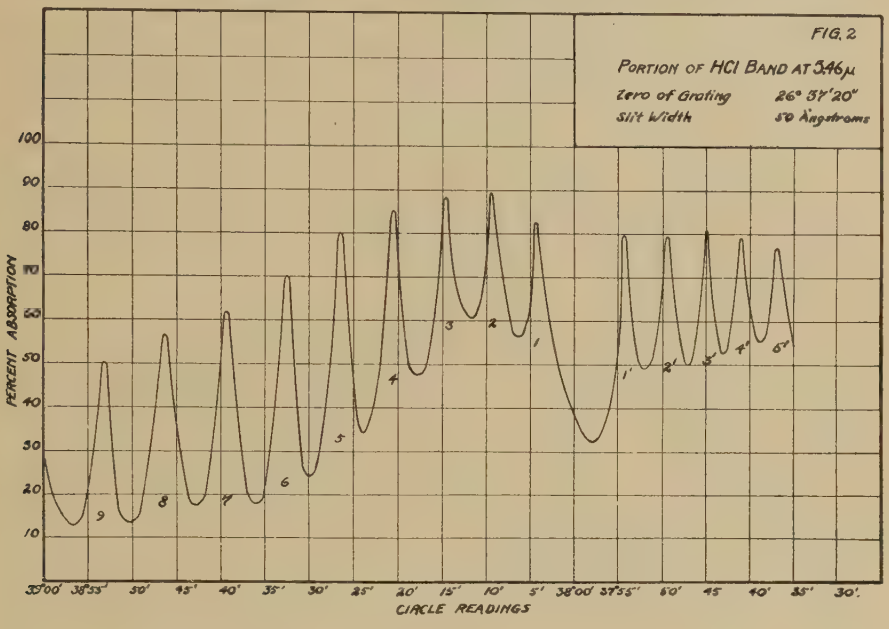
Two absorption cells were used. Both were of precisely the same dimensions and placed immediately in front of the slit S_1. One cell was filled with the gas to be investigated and the other with air from which the CO_2 and water vapor had been removed by pumping the air through two wash bottles of granular KOH in series and then through two of concentrated H_2SO_4. The cells were 15 cm long and about 9 cm in diameter and were mounted so that they could be placed alternately in the path of the radiation from the glower. The ends of the cells were closed with thin mica windows clamped to the ends of the cells by a brass ring and made practically gas tight by thin rubber gaskets of dental dam.

METHOD AND RESULTS

The first work done on the present problem was on the HCl band at 3.46μ with the idea of calibrating the spectrometer and testing the accuracy of the method. The HCl was formed by dropping concentrated sulphuric acid on C.P. sodium chloride and washing the gas through water saturated with HCl and then through two wash bottles of concentrated sulphuric acid to dry it. It was then passed through the absorption chamber and finally disposed of by absorption in water. The absorption chamber was adjudged saturated with HCl when all the gas emitted from the cell was absorbed by the water, but a slow stream of gas was kept flowing through the cell during the taking of the observations.

The deflections were obtained by opening and closing a shutter immediately in front of the slit S_1. Two deflections were taken with the HCl in the path of the beam and then two with the cell containing dry air and then two more with HCl and so on alternately until 6 deflections were obtained with HCl in the path and four with dry air. This method was used because of a slow but steady drift of the galvanometer zero toward the position of less sensitivity during a large share of the work. The absorption percentage was obtained by subtracting the deflections obtained with HCl in the path from those with dry air and dividing the difference by the latter and expressing the result in percent.

Fig. 2 shows the curve obtained for a portion of the HCl band including the maxima numbering from 9 to 5′ and Fig. 3 the curves for a few separate peaks obtained from a single set of data, with spectrometer



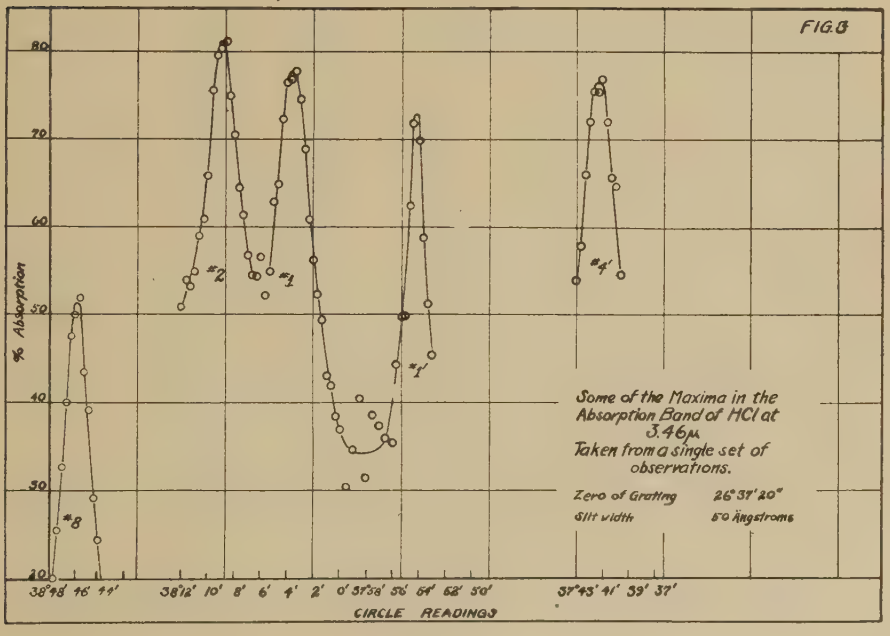


FIG. 3
% Absorption
Some of the Maxima in the Absorption Band of HCl at 3.46μ
Taken from a single set of observations.
Zero of Grating 26° 37′ 20″
Slit width 50 Ångstroms
CIRCLE READINGS

settings for the latter curve made at every 20″ of arc. Using a grating constant of 2887.6 the position of all the peaks agreed with the results obtained by Colby and Myers to within 25 ängstroms while most of them agreed within 10 ängstroms.

The same absorption cells were then used for carbon monoxide after the brass cylinders had been rebored to clean them and fresh mica windows substituted. The CO was formed by dropping 90 percent C.P. formic acid on concentrated C.P. sulphuric acid which was kept at a temperature of 85°C. on an oil bath. The gas was then washed through a concentrated solution of KOH and through two bottles of conc. H_2SO_4 to remove any possible CO_2 and any water vapor formed in the reaction

$$HCOOH+H_2SO_4=CO+H_2O+H_2SO_4$$

It was not thought necessary to maintain a flow of the gas through the absorption chamber during the process of taking observations but the gas was run through the cell for about an hour just previous to taking each set of readings. The gas flowing out of the cell was passed through a safety lamp and burned, the cell being considered saturated with CO when the flame at the lamp no longer exhibited an inner cone of combustion which would be evidence of an admixture of air with the CO.

Settings were made every 30 sec. over the central portion of the band and the percentage of absorption for each setting calculated in the same manner as for HCl. Fig. 4 shows the curve obtained, which is a doublet with maxima at 4.600(1) and 4.728(5)μ with the center of the band at 4.6643μ, agreeing extremely well with Burmeister's results. There is very little if any evidence of fine structure of the band as it was hoped we might find. For one set of observations the thermopile slit was narrowed until it had a width of 50″ and included about 40 ängstroms with settings made every 20″ or about every 17 ängstroms but no better evidence of fine structure was obtained. All of the curve has been gone over twice and the major portion four times with an agreement between separate observations on a single setting averaging better than 1 percent. Although the plotted points for the curve of Fig. 4 are not shown, none of them varies from the curve as drawn by more than one per cent. This is a better agreement than was obtained for the HCl curve as is in evidence from Fig. 3 and was due in part to a better technique but more particularly to much better steadiness of the galvanometer.

CONCLUSIONS

Though no fine structure for the band was found the position of the maxima at 4.600(1)μ and at 4.728(5)μ enables us to calculate the

moment of inertia of the CO molecule by making use of the formula already referred to, namely

$$I = \frac{RT}{4\pi^2 \nu_r^2 N}$$

Taking R as 8.32×10^7, T as 293° abs. N as 60.6×10^{22}, and $2\nu_r$ obtained from the equation

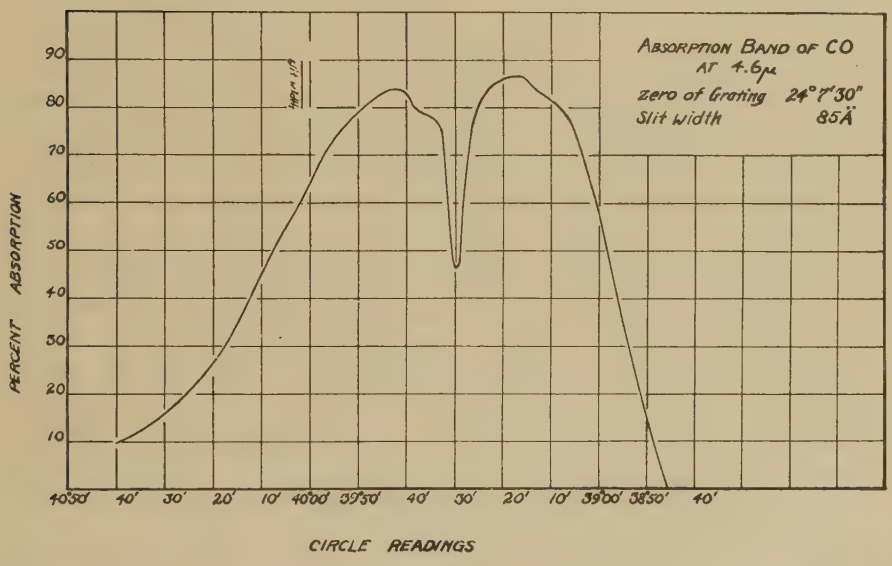
$$2\nu_r = c\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)$$

as 1.66×10^{12} we get the value of I to be 14.9×10^{-40}.

This value of I may be used in the equation

$$I = \frac{mm'}{m+m'} l^2$$

FIG. 4



to determine the distance l between atomic centers in the CO molecule, where m and m' are the masses of the carbon and the oxygen atoms respectively. We get from this equation l to be 1.15×10^{-8} cm.

These numerical results agree very well with those given by Eucken[13] in which he calculates the value of the dimensions of the CO molecule by four different methods. From the separation of the maxima of the infra-red double bands and for which he does not give the experimental authority he gets 14.7×10^{-40}; from the separation of the lines in the visible band spectrum 15.8×10^{-40}; from the vapor pressure curve and

[13] Zeits. für Electrochemie, *26*, p. 377; 1920.

C_r, the heat of rotation of the molecule, 14.7×10^{-40}; and from the molecular model of Fraulein Gerda Laski[14] 14.1×10^{-40}. He obtains from these values of I 1.16×10^{-8} cm as the most probable distance between atomic centers, a result which is in very close agreement with our value.

C. E. Guye and R. Rudy[15] give for the molecular diameter of CO the value of 3.36×10^{-8} obtained from viscosity measurements taken from results in "constantes physiques de la Societe francaise de Physique." By applying the formula for the rotation of an electric discharge in a gas

$$\nu=\frac{eH}{12\pi s^2 m M}$$

where e and m are the charge and mass respectively of the positive ion under the simultaneous action of two uniform fields, an electric field parallel to the y axis and a magnetic field M parallel to the z axis, M the number of molecules per unit volume, and s the radius of the molecule, the same authors arrive at the value of 3.88×10^{-8} for the diameter of the molecule. J. Robinson[16] gives 3.50×10^{-8} as the value obtained from measurements of the absorption of cathode rays.

It is of some interest to attempt a correlation between the value of the distance between atomic centers as given above and the molecular diameter as given by the last three methods. The diameter of the molecule based on the above collision phenomena may be taken as equal to the nearest distance of approach of two similar molecules. W. H. Westphal (ZS. für Physik *4*, 254; 1921) has calculated the values of a and r_0 for Chlorine, Bromine and Iodine molecules where a is the radius of the molecule and r_0 is the nearest distance of approach. He arrives at the following ratios

$$\frac{r_0}{a}(\mathrm{Cl})=\frac{1.27}{1.05}=1.21$$

$$\frac{r_0}{a}(\mathrm{Br})=\frac{1.355}{1.19}=1.14$$

$$\frac{r_0}{a}(I)=\frac{1.49}{1.40}=1.06$$

If we plot the value of these ratios against the molecular weights we get a linear relation which gives 1.25 as the value of this ratio for a molecular weight of $16+12=28$. Now let us take as the diameter of

[14] Phys. Zeitsch., *20*, p. 269; 1919.
[15] Comptes Rendus, *174*, No. 6, p. 382; 1922.
[16] Proc. U. Durham Phil. Soc., *3*, Pt. 4; 1915.

the spherical molecule the longest diameter of the parallelopiped formed by the valence electrons of the Lewis-Langmuir molecular model for CO. We get for this diameter 2.83×10^{-8} cm, taking the parallelopiped to be formed of two cubes in the centers of which are the *C* and *O* nuclei respectively and taking the distance between nuclei to be 1.15×10^{-8} cm. Now if we multiply the value of $2a$ so obtained by the ratio given above, we get for the diameter of the effective sphere 3.54×10^{-8} cm. The average of the three values given above for this quantity is 3.58×10^{-8}. On the basis of the Bohr theory a similar result may be arrived at from the idea of elliptical orbits and the theory that these orbits are more or less interpenetrating.

From the suggestion first offered by Ehrenfest[17] that the value of the spacing between the separate maxima in the molecular band spectra might be expressed by the equation

$$d\nu = \frac{h}{4\pi^2 I}$$

where h is Planck's constant and I the moment of inertia of the molecule we get $d\nu$ for CO at 4.66μ to be about 80 angstroms. On this basis apparently we should have found some evidence of the fine structure of the band. On the short wave side of the HCl band at 3.4μ the peaks are about 200 angstroms apart and were found by Imes without difficulty, using a slit width of 100 A. or half the separation between the maxima. In Figs. 2 and 3 of this paper these maxima are shown to be very distinct with a slit width 50 A. Although, as before stated, the thermopile slit was decreased in width to 40 A. or about one half the calculated value of the separation between the maxima for part of the work on CO, no evidence of the fine structure was found. This must lead to one of two conclusions. Either the maxima are much closer together than the above equation would indicate or the resolving power of the spectrometer approaches a critical value beyond which decreased slit width does not increase its value in the same ratio.

On examination of the carbon monoxide curve it is evident that there are slight minima, one on each side of the band center. The decrease in absorption of each of these points is slight but there is little doubt as to its occurrence. It is, however, difficult to account for these minima. It is hardly probable that they are due to irregularities in the grating surface. On the other hand it is not evident as to what molecular behavior would give rise to their appearance on the basis of our present knowledge of the origin of molecular spectra.

[17] Verh. d. D. Phys. Ges., *15*, p. 451; 1913.

In conclusion I wish to express my thanks to Dr. F. C. Blake of this department who suggested the problem and who has aided me materially by his interest and suggestions, and to Mr. Brooks, the department mechanician, for his painstaking work in the building of the apparatus.

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AUTOBIOGRAPHY

I, Erwin Foster Lowry, was born in Ridgeway, Michigan, January 22, 1891. I received my secondary education in the public and high schools of Michigan and New York; my undergraduate education at the Ohio Wesleyan University from which I obtained the degree of Bachelor of Arts in 1914 and the degree of Master of Arts in 1916. In 1914-15 I held the position of Assistant in Physics at Ohio Wesleyan and that of Instructor in Physics during 1915-16. I then went to the University of Pittsburgh where I was Instructor in Physics from 1916 to 1920. I was Instructor in Physics at the Ohio State University from the fall of 1920 to June, 1923 and received the degree of Doctor of Philosophy from that institution in August, 1923.